

Ferromagnetic insulating state in tensile-strained LaCoO_3 thin films

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(Dated: February 25, 2013)

Abstract

With local density approximation + Hubbard U (LDA+ U) calculations, we show that the ferromagnetic (FM) insulating state observed in tensile-strained LaCoO_3 epitaxial thin films is most likely a mixture of low-spin (LS) and high-spin (HS) Co, namely, a HS/LS mixture state. Compared with other FM states, including the intermediate-spin (IS) state (*metallic* within LDA+ U), which consists of IS Co only, and the insulating IS/LS mixture state, the HS/LS state is the most favorable one. The FM order in HS/LS state is stabilized via the superexchange interactions between adjacent LS and HS Co. We also show that Co spin state can be identified by measuring the electric field gradient (EFG) at Co nucleus via nuclear magnetic resonance (NMR) spectroscopy.

PACS numbers: 75.50.Cc, 75.70.Ak, 76.60.Gv

19 Perovskite-structure oxides have been proven a fertile area in condensed matter physics.
 20 They exhibit amazing properties, including ferroelectricity, ferromagnetism, colossal magne-
 21 toresistance (CMR), and multiferroics (simultaneous ferroelectricity and ferromagnetism),
 22 as a consequence of their spin, lattice, charge, and orbital degree of freedom. Advances in
 23 thin-film growth techniques have even brought more promising potentials for their future
 24 application, as their properties can be engineered via epitaxial strains. A few examples
 25 include strontium titanate (SrTiO_3), ferroelectric in tensile-strained thin film while para-
 26 electric in bulk,¹ lanthanum titanate (LaTiO_3), conducting in compressive-strained thin
 27 film while insulating in bulk,² and Europium titanate (EuTiO_3), in which multiferroics in-
 28 duced by tensile strains has been observed.³ As to lanthanum cobaltite (LaCoO_3), a diamag-
 29 netic insulator in bulk at low temperatures ($T < 35$ K), a ferromagnetic (FM) *insulating*
 30 state has been observed in tensile-strained thin films, e.g. LaCoO_3 grown on SrTiO_3 or
 31 $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$, at $T < 85$ K,⁴⁻¹³ while the ferromagnetism induced by com-
 32 pressive strains, e.g. LaCoO_3 grown on LaAlO_3 , is not conclusive.^{5-7,14} Two questions arise
 33 immediately: (1) Given that there are six $3d$ electrons in Co^{3+} , which can thus have a to-
 34 tal electron spin $S = 0, 1$, or 2 , refereed to as low-spin (LS), intermediate-spin (IS), and
 35 high-spin (HS) state, respectively, what is the spin state of Co in FM LaCoO_3 thin films, in
 36 contrast to the LS Co in diamagnetic bulk? (2) What leads to the formation of FM order in
 37 LaCoO_3 thin films? After all, FM *insulators* are rarely seen. So far, all first-principles cal-
 38 culations have only found FM *metallic* LaCoO_3 thin films with all Co ions in IS state,^{11,15,16}
 39 a prediction clearly inconsistent with transport measurements.⁶

40 While finite Co spin induced by tensile strains in LaCoO_3 thin films has just started
 41 attracting attention, finite Co spin induced by thermal excitation in bulk LaCoO_3 has been
 42 a highly controversial issue for decades.^{17,18} With LS Co at $T < 35$ K, bulk LaCoO_3 becomes
 43 a paramagnetic insulator with finite Co spin at about 90 K. Such a spin-state crossover in
 44 the temperature range of 35–90 K was first suggested to be a LS-HS crossover¹⁹⁻²¹ but was
 45 later suggested to be LS-IS based on a local density approximation + Hubbard U (LDA+ U)
 46 calculation.²² Since then, both scenarios have received supports from various experimental
 47 and theoretical works, but a consensus is not yet achieved (see Ref. 23 for a brief review).
 48 A study regarding LaCoO_3 thin films may also help understanding LaCoO_3 bulk from a
 49 different perspective. In this paper, we investigate the Co spin state in tensile-strained thin

50 films and the formation of FM order via a series of LDA+ U calculations. While LDA+ U has
 51 been frequently used to study cobaltites and Co spin state, the choice of Hubbard U can be
 52 an issue. It has been shown that under the same lattice parameter, the Hubbard U affects the
 53 total energy and the determination of ground state.¹⁶ A well justified Hubbard U determined
 54 by first principles would thus be necessary for finding out the the actual ground state. In
 55 this paper, we compute the Hubbard U parameters of Co in all spin states self-consistently
 56 with a linear response approach.^{24–26} This method has successfully found the ground state
 57 of iron-bearing magnesium silicate (MgSiO₃) perovskite at a wide range of pressure.²⁶ Both
 58 the plane-wave pseudopotential (PWPP) method²⁷ implemented in QUANTUM ESPRESSO
 59 codes²⁸ and the augmented plane wave + local orbitals (APW+lo) method²⁹ implemented
 60 in WIEN2k codes³⁰ are used. As shall be pointed out later, the orbital occupancies of Co in
 61 thin films are different from those in bulk, due to their different symmetries. We therefore
 62 compute the electric field gradient (EFG) tensor at Co nucleus, V_{zz} , with WIEN2k, to see
 63 whether the Co spin state in thin films can be identified via EFG, as demonstrated in bulk.²³

64 The pseudocubic lattice parameter of bulk LaCoO₃ ($R\bar{3}c$ symmetry) is about 3.81 Å
 65 at $T \sim 5$ K.^{31,32} To model tensile-strained LaCoO₃ thin films via bulk calculations, we
 66 constrain the in-plane pseudocubic lattice parameters a_{pc} and b_{pc} of the hypothetical bulk
 67 to 3.899 Å (the lattice constant of cubic SrTiO₃ at low temperatures),³³ set $\alpha = \beta = \gamma =$
 68 90° , and optimize the out-of-plane pseudocubic lattice parameter (c_{pc}). Due to the lack of
 69 accurate information regarding CoO₆ octahedral rotation in thin-film LaCoO₃ in the low-
 70 temperature FM phase, we consider two extreme cases shown in Fig. 1: (a) cube-on-cube,
 71 namely, no CoO₆ octahedral rotation degree of freedom, and (b) full CoO₆ rotation degree
 72 of freedom subject to the above-mentioned constraints. We also consider several magnetic
 73 configurations shown in Fig. 2: (a) all Co ions in LS state, (b) all Co ions have the same
 74 magnetic moment aligned in FM order, and (c) a mixture state with LS Co surrounded by
 75 magnetic Co (and vice versa) aligned in FM order. The configuration shown in Fig. 2(c) is
 76 a legitimate postulate, as the observed magnetization in LaCoO₃ thin films rarely exceeds
 77 $0.85 \mu_B/\text{Co}$.^{4–11} For the configuration in Fig. 2(b), a convergent wave function for HS state
 78 cannot be obtained; only IS state can be found. For the configuration in Fig. 2(c), both
 79 HS/LS and IS/LS mixture state can be obtained. The self-consistent Hubbard U parameter
 80 (U_{sc}) of LS and IS Co are 7.0 eV, while the HS/LS state has $U_{sc}^{(HS)} = 5.4$ and $U_{sc}^{(LS)} = 7.2$

eV.³⁴ The dependence of U_{sc} on c_{pc} is negligible. To demonstrate how the choice of Hubbard U can affect the determination of ground state, we also present the result obtained using a constant $U = 7$ eV for all Co in our PWPP calculations. In tensile-strained LaCoO_3 thin films, CoO_6 octahedra possess tetragonal symmetry, namely, longer Co–O distance on the xy plane, regardless of CoO_6 rotation, as will be discussed in the next paragraph. In tetragonal symmetry (D_{4h}), the spin-down electron of HS Co occupies d_{xy} orbital, and the spin-down electrons of IS Co occupy d_{xz} and d_{yz} orbitals, as shown in Fig. 2(d). Such orbital occupancies are very different from those in bulk LaCoO_3 , in which CoO_6 octahedra have trigonal symmetry (D_{3d}), with the $[111]$ direction being the high-symmetry axis. In bulk LaCoO_3 , the spin-down electron of HS Co occupies the d_{z^2} -like orbital oriented along the $[111]$ direction, and the IS Co spin-down electrons occupy the doublet with 3-fold rotation symmetry about the $[111]$ direction.²³

The optimized out-of-plane pseudocubic lattice parameter (c_{pc}) of each FM state and associated relative energy (ΔE) and band gap (E_{gap}) are listed in Tables I-II. Regardless of CoO_6 rotation, the HS/LS mixture state (with U_{sc}) is the most stable FM state given by the PWPP method (Table I).³⁵ While the choice of $U = 7.0$ eV makes HS/LS state less favorable in PWPP calculations, APW+lo calculations still find HS/LS the most stable FM state (Table II). Both PWPP and APW+lo methods open an energy gap for HS/LS state, consistent with transport measurements.⁶ Also, the presence of HS Co is consistent with recent x-ray magnetic circular dichroism (XMCD) and x-ray absorption spectroscopy (XAS) spectra.^{9,10} In contrast, the IS state is never the most favorable FM state, regardless of the computation method and CoO_6 rotation. Its partially filled bands formed by partially occupied d_{z^2} and $d_{x^2-y^2}$ orbitals in IS Co lead to a nonzero density of state at the Fermi level. When the IS Co concentration is reduced to 50%, an energy gap is opened in APW+lo calculations (Table II), while PWPP calculations still give a conducting IS/LS state (Table I). Such a difference is likely to result from the way that the Hubbard U is applied. In PWPP, the Hubbard U is applied to the projection of the total wave function onto Co $3d$ orbitals;²⁴ in APW+lo, the Hubbard U is directly applied to the $3d$ orbitals within the muffin-tin radius of Co (1.9 bohr). Insulating or not, the IS/LS state is highly unlikely; its energy is even higher than that of IS state. One more thing worthy of mention is that the Co–O distance ($d_{\text{Co-O}}$) and Co–O–Co angle obtained in our calculation are different

from those estimated in Ref. 5, where a constant $d_{\text{Co-O}} = 1.93 \text{ \AA}$ is assumed (regardless of compressive or tensile strains), and an Co–O–Co angle of 176° is estimated for LaCoO_3 grown on SrTiO_3 . In our PWPP calculation with U_{sc} and CoO_6 rotation, the HS/LS state has $d_{\text{Co(HS)-O}} = 2.015$ and 1.872 \AA , $d_{\text{Co(LS)-O}} = 1.922$ and 1.886 \AA , and Co–O–Co angles of 163.8° and 156.6° , on the xy plane and along the z axis, respectively. Even for the IS state suggested by Ref. 5, we have $d_{\text{Co(IS)-O}} = 1.973$ and 1.939 \AA , and Co–O–Co angles of 162.3° and 154.9° , on the xy plane and along the z axis, respectively.

Other than the total energy, structural properties can be a useful criterion to determine which FM state favors tensile strains ($c_{\text{pc}}/a_{\text{pc}} < 1$). Starting with the structures listed in Table I with CoO_6 rotation, we perform full structural optimization (at constrained volume) via variable cell-shape damped molecular dynamics.³⁶ All lattice parameters, including α , β , and γ , are optimized, so the final structures only experience hydrostatic pressures. With α , β , and γ slightly deviated from 90° , the IS state has $c_{\text{pc}}/a_{\text{pc}} > 1$, while all other states remain $c_{\text{pc}}/a_{\text{pc}} < 1$ (but IS/LS state still has a $c_{\text{pc}}/a_{\text{pc}}$ larger than that of HS/LS state), as shown in Table III. The larger $c_{\text{pc}}/a_{\text{pc}}$ ratio associated with IS Co is a direct consequence of its occupied d_{xz} and d_{yz} orbitals (by spin-down electrons), which elongate the Co–O distance along the z -direction. In contrast, the fully optimized HS/LS state has $c_{\text{pc}}/a_{\text{pc}} = 0.969$, in great agreement with $c_{\text{pc}}/a_{\text{pc}} = 0.967$ observed in experiments.⁶

A significant part of cobalt-spin controversy arises from the difficulty in directly measuring the total electron spin of Co. Such difficulty, also appearing in other spin systems, can be resolved by comparing the calculated and measured EFGs.^{23,26,37} So far, insulating FM state has been observed in LaCoO_3 thin films with a_{pc} ranging from 3.84 to 3.90 \AA .^{5,8} In these thin films, the magnetic Co concentration and Co–O distance may be different, which can lead to slightly different EFG for Co in the same spin state. To find out possible upper and lower limits of HS and IS Co EFG, we compute them in two extreme cases: (1) thin films with $a_{\text{pc}} = 3.899 \text{ \AA}$ and 50% of magnetic Co, namely, the HS/LS and IS/LS states listed in Tables I and II, and (2) single isolated HS or IS Co in an array of LS Co in a fully relaxed structure with $a_{\text{pc}} \sim 3.81 \text{ \AA}$, where the orbital occupancies of isolated HS and IS Co are maintained in tetragonal symmetry [Fig. 2(d)]. In these APW+lo calculations, IS Co does not lead to a metallic state, in contrast to bulk LaCoO_3 (D_{3d} symmetry).²³ Different choices of Hubbard U have been adopted as well (5 eV, 7 eV, and U_{sc}). The results of all

143 these calculations show that the EFG mainly depends on the spin state: $14.7 < V_{zz}^{(\text{HS})}/(10^{21}$
 144 $\text{V/m}^2) < 19.9$ and $-14.6 < V_{zz}^{(\text{IS})}/(10^{21} \text{ V/m}^2) < -8.0$. The quadrupole frequency, $\nu_Q \equiv$
 145 $3eQ|V_{zz}|/2I(2I-1)\hbar$, can thus be easily predicted, with $Q = 0.42 \times 10^{-28} \text{ m}^2$ and $I = 7/2$
 146 for ^{59}Co nucleus. Based on the range of $V_{zz}^{(\text{HS})}$ and $V_{zz}^{(\text{IS})}$, we conclude that in insulating
 147 LaCoO_3 thin films, a measured ν_Q via nuclear magnetic resonance (NMR) spectroscopy
 148 within $\sim 8.2 \pm 2.4 \text{ MHz}$ can be a strong evidence for IS Co, and a measured ν_Q within
 149 $\sim 12.6 \pm 1.9 \text{ MHz}$ should indicate HS Co.

150 Analysis of electronic structures can help developing a physical understanding for the FM
 151 order in HS/LS state, whose projected density of states (PDOS) are shown in Fig. 3. The
 152 case with $U = 7 \text{ eV}$ and no CoO_6 rotation is presented, as the main features in PDOS are
 153 not sensitive to the choice of U and CoO_6 rotation. Extracted from Fig. 3(a), both HS and
 154 LS Co have nonzero magnetic moment: 2.97 and $0.56 \mu_B$, respectively. The FM order is
 155 established via the superexchange interaction between HS and LS Co, as described by the
 156 Goodenough-Kanamori rule,^{17,38–40} which states that the superexchange interaction between
 157 two cations (with or without a shared anion) is ferromagnetic if the electron transfer is from
 158 a filled to a half-filled orbital or from a half-filled to an empty orbital. Indeed, for the HS/LS
 159 state, electrons transfer from the filled d_{xz} and d_{yz} orbitals of LS Co to the half-filled d_{xz}
 160 and d_{yz} orbitals of HS Co via the oxygen in between, and also from the half-filled e_g (d_{z^2}
 161 and $d_{x^2-y^2}$) orbitals of HS Co to the empty e_g orbitals of LS Co, as depicted in the inset of
 162 Fig. 3(b). The PDOS shown in Fig. 3(b) confirms this model: the finite spin-up e_g electrons
 163 localized at the LS Co site (transferred from the HS Co site) and the finite spin-down d_{xz}
 164 and d_{yz} electrons localized at the HS Co site (transferred from the LS Co site). Such electron
 165 transfers have been also described via a *configuration fluctuation* model,^{20,21} which further
 166 suggests that the interchange of spin states (without net transfer of charge) led by electron
 167 transfers stabilizes the FM order in this HS/LS states.

168 The above-mentioned superexchange interaction can be visualized via electron spin den-
 169 sity $s(\mathbf{r}) \equiv \rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})$, where $\rho_{\uparrow}(\mathbf{r})$ and $\rho_{\downarrow}(\mathbf{r})$ are spin-up and spin-down electron density,
 170 respectively. Figure 4(a) shows $s(\mathbf{r})$ corresponding to the configuration with all HS Co
 171 magnetic moments aligned (same as the configuration in Fig. 3). The nonzero magnetic
 172 moments localized at LS Co sites (with e_g character), aligned with the HS Co magnetic
 173 moments, are consistent with the PDOS shown in Fig. 3. When the magnetic moment of

one HS Co in a 40-atom supercell is flipped [Fig. 4(b)], the alignment of magnetic moments is altered, and so is the condition that allows configuration fluctuation [inset of Fig. 3(b)]. The spin density at surrounding LS Co sites is thus significantly affected. One flipped HS Co spin (in a 40-atom cell) increases the total energy by 195 meV/supercell. Flipping one more HS Co spin, so the total magnetization per supercell becomes zero, further increases the total energy by 78 meV/supercell. With CoO_6 rotation, the energy increases associated with one and two flipped HS Co spins are 96 and 34 meV/supercell, respectively. These results indicate that the magnetic moment of HS Co in the HS/LS state should align at low temperatures.

While our calculations have shown that HS/LS state is the most favorable state among the ferromagnetic states being considered, magnetic state in actual LaCoO_3 thin films can be more complicated. The magnetization observed in experiments rarely exceeds $0.85 \mu_B/\text{Co}$,⁴⁻¹¹ smaller than that of the HS/LS mixture ($2 \mu_B/\text{Co}$). Such a magnetization suggests that the HS Co population should be smaller than 50%. In fact, XAS spectra combined with atomic multiplet calculations have suggested that LaCoO_3 thin film on SrTiO_3 consists of about 64% of LS Co and 36% of HS Co.¹⁰ Given that the FM order is achieved via the superexchange interaction within the HS-LS-HS Co configuration shown in Fig. 2(c), one can thus expect ferromagnetic HS/LS domain and nonmagnetic LS domain coexist in tensile strained thin films, as observed using magnetic force microscopy (MFM).⁷ Also, since HS/LS state favors larger in-plane lattice parameter, thin films with larger in-plane lattice parameters can be expected to have larger HS/LS domain, and thus larger magnetization, consistent with the increase of magnetization with lattice parameter observed in experiment.⁵

In summary, we use LDA+ U calculations to show that the ferromagnetic insulating state in tensile-strained LaCoO_3 thin films is most likely a mixture of HS and LS Co. Among all the ferromagnetic states studied in this paper (HS/LS, IS/LS, and IS), the insulating HS/LS mixture state is the most favorable one, energetically and structurally. Its FM order is established via the superexchange interaction between LS and HS Co. We also show that cobalt spin states in LaCoO_3 thin films could be identified via NMR spectroscopy.

This work was primarily supported by the MRSEC Program of NSF grants DMR-0212302 and DMR-0819885, and partially supported by EAR-081272 and EAR-1047629. P.B. was

supported by the Austrian Science Fund (SFB F41, "ViCoM"). Calculations were performed at the Minnesota Supercomputing Institute (MSI). We thank C. Leighton for valuable discussions.

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- ³⁴ In this paper, U_{sc} is extracted from a series of LDA+*U* ground states associated with different trial *U*, as detailed in the supplemental material of Ref. 26 (<http://link.aps.org/supplemental/10.1103/PhysRevLett.106.118501>). In our earlier work on LS LaCoO₃ (Ref. 27), the Hubbard *U* for LS Co (~ 8.3 eV) was extracted from the LDA ground state, as detailed in Ref. 24.
- ³⁵ In our calculations with constrained in-plane lattice parameters ($a_{\text{pc}} = b_{\text{pc}} = 3.899$ Å), a HS state with G-type antiferromagnetic (AFM) order can be obtained, and its energy is lower than that of the HS/LS state. Given the neglect of finite thickness, the possible uncertainty of energy given by LDA+*U* method, and the fact that AFM thin film is not observed in experiments, we limit our discussions on the available FM states (IS, IS/LS, and HS/LS).
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TABLE I. Optimized out-of-plane pseudocubic lattice parameter (c_{pc}) and associated relative energy (ΔE) and energy gap (E_{gap}) of each FM state in tensile-strained LaCoO_3 thin film (PWPP method).

	No CoO_6 rotation			Full CoO_6 rotation		
	c_{pc} (\AA)	ΔE (eV/f.u.)	E_{gap} (eV)	c_{pc} (\AA)	ΔE (eV/f.u.)	E_{gap} (eV)
LS	3.865	0.35	0.54	3.660	0.32	1.24
IS	3.785	0.20	metal	3.785	0.19	metal
IS/LS	3.720	0.35	metal	3.680	0.29	metal
HS/LS (U_{sc})	3.685	0.00	0.92	3.680	0.00	0.90
HS/LS ($U = 7$ eV)	3.700	0.29	1.12	3.695	0.29	0.90

TABLE II. Optimized c_{pc} and associated ΔE and E_{gap} of each FM state (APW+lo method, with CoO_6 rotation).

	c_{pc} (\AA)	ΔE (eV/f.u.)	E_{gap} (eV)
LS	3.660	0.37	1.72
IS	3.741	0.18	metal
IS/LS	3.672	0.29	0.59
HS/LS ($U = 7$ eV)	3.686	0	1.52

TABLE III. Fully optimized pseudocubic lattice parameters of each FM state at the volume as in Table I (with CoO_6 rotation).

	$a_{\text{pc}}, b_{\text{pc}}$ (\AA)	c_{pc} (\AA)	$c_{\text{pc}}/a_{\text{pc}}$
IS	3.848	3.893	1.012
IS/LS	3.847	3.778	0.982
HS/LS (U_{sc})	3.863	3.745	0.969
HS/LS ($U = 7$ eV)	3.865	3.757	0.972

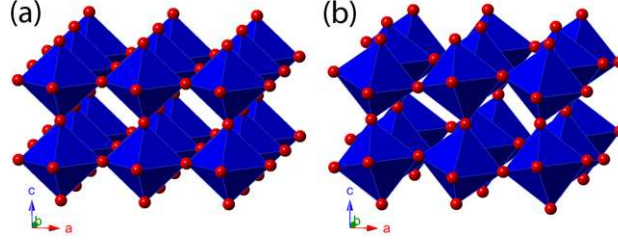


FIG. 1. (color online). Possible atomic structures of LaCoO_3 thin film (La is not shown) subject to constrained in-plane lattice parameters. (a) Cube on cube, no CoO_6 octahedral rotation; (b) full octahedral rotation degree of freedom.

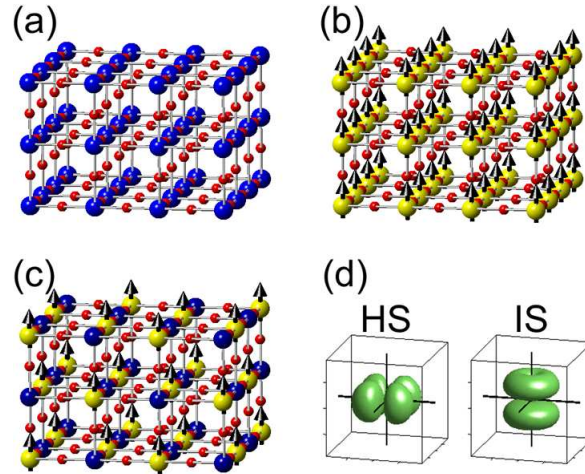


FIG. 2. (color online). (a)-(c) Possible magnetic configurations in LaCoO_3 epitaxial thin film (La is not shown). The arrows denote for nonzero magnetic moments, either IS or HS. (a) LS state; (b) HS or IS state in FM order; (c) HS/LS or IS/LS mixture state in FM order. (d) The $3d$ orbitals occupied by the spin-down electrons of HS and IS Co.

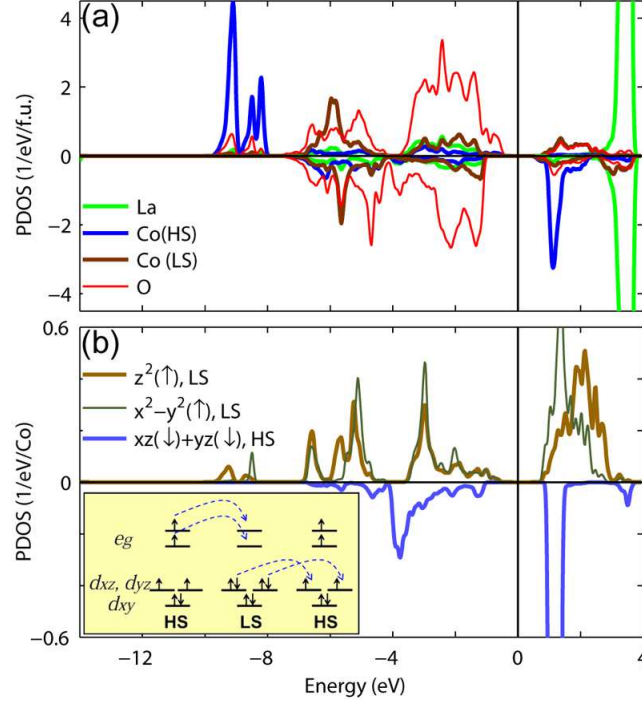


FIG. 3. (color online). Projected density of states of ferromagnetic HS/LS state (no CoO_6 rotation, $U = 7$ eV) onto (a) each atomic site, and (b) some of the Co 3d orbitals. The inset in (b) shows the electron transfer between HS and LS Co.

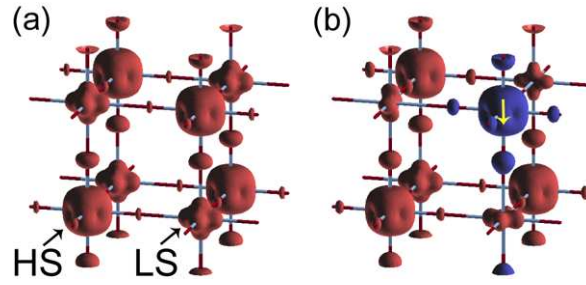


FIG. 4. (color online). Spin density, $s(\mathbf{r})$, of HS/LS state (no CoO_6 rotation, $U = 7$ eV) with (a) all HS Co magnetic moments aligned, and (b) one HS Co magnetic moment flipped downward (indicated by arrow). The isosurface values are 0.02 (red) and -0.02 (blue).